

gen-bond formation.² Moreover, several groups^{8,9,47} have reported hydrogen bonding between HSiCl_3 and oxygen bases, although the evidence presented is rather sketchy. Certainly, several hydrogen-bonded complexes of the carbon analogue, chloroform, have been isolated and characterized in argon matrices.^{3,48} Hence, the possibility of a weak hydrogen bond involving the Si-H bond and the lone electron pair on the base is present, and the spectral data near 2200 cm^{-1} support this. It is noteworthy that a red-shifted Si-H band was not observed when $(\text{CH}_3)_2\text{O}$ was codeposited with HSiCl_3 . Dimethyl ether is a weaker base than the amines,⁴⁹ and hydrogen-bond formation would be energetically less favored.

One would also expect that the Cl-Si-H bending mode to blue shift as has been seen for many other hydrogen-bonded complexes. However, the intensity of the bending mode is usually much less than that of the stretching mode. Since the red-shifted stretching mode was itself quite weak, the blue-shifted bending mode might well escape detection. The remaining acid and base modes in a weak hydrogen-bonding interaction are generally very weakly perturbed and would not be observed here. Consequently, the red-shifted Si-H stretching mode suggests formation of a second isomeric complex in which a hydrogen bond is formed between the Si-H group and the amine (species B in Figure 4). However, lack of observation of the perturbed bending mode makes this assignment tentative.

The observation, at least tentatively, of two different complexes between the amine bases and HSiCl_3 suggests that there are at least two local minima on the complete potential energy surface for the complex. Whether there is a barrier to interconversion between the two isomers in the gas phase or in solution is not clear; Ozin et al.³⁸ only reported a single structure. However, the argon matrix environment, which condenses rapidly around the complex during the deposition process, could well stabilize both isomers and prevent isomerization to the more stable form, presumably the coordination complex.

In the $\text{NH}_3/\text{HSiCl}_3$ experiments, additional bands were observed at high NH_3 concentrations and assigned to a larger ag-

gregate. Most likely, this is a 2/1 complex, which can be envisioned as forming through the addition of a second NH_3 to the initial 1/1 complex. It is difficult to determine the structure of the 2/1 complex, which might either be cis or trans octahedral or involve the two sites of coordination seen for the two different 1/1 complexes. The study^{11,12} of the 2/1 complex of pyridine with HSiCl_3 showed a strongly red-shifted Si-H stretch, and a strongly blue-shifted Cl-Si-H bending mode, indicative of hydrogen bonding (although the authors did not make this suggestion). It may well be that one pyridine coordinates to the silicon and the second pyridine is hydrogen-bonded to the Si-H group. If so, a similar structure might be suggested for the 2/1 complex observed here, but the data do not permit a more definitive conclusion.

Previous studies have all demonstrated that substitution of a methyl group on silicon significantly reduces its reactivity and ability to form complexes.^{16,17,44} The experiments here involving codeposition of CH_3SiCl_3 with either NH_3 or $(\text{CH}_3)_3\text{N}$ led to very little, if any, product formation, consistent with this view. Likewise, codeposition of HSiCl_3 with acetone and with acetonitrile did not lead to the formation of a detectable product, which is probably due to their lower basicities, particularly for CH_3CN .

Summary

The codeposition of a series of bases containing nitrogen and oxygen donor atoms with HSiCl_3 has led to the formation of isolated 1/1 molecular complexes. In each case, evidence pointed to the formation of coordination complexes, in which the donor atom of the base interacts with the silicon center on HSiCl_3 . These complexes were characterized by a distinct blue shift of the Si-H stretching mode, a red shift of the Cl-Si-H bending mode, and red shifts of the Si-Cl stretches. These complexes appear to be trigonal bipyramidal around the central silicon, with the base in an axial position and the hydrogen in an equatorial position. In addition, when amines were codeposited with HSiCl_3 , evidence was found to tentatively indicate that a second, isomeric form of the complex was isolated, in which the base hydrogen bonded to the Si-H bond. These complexes were characterized by a distinct red shift and broadening of the Si-H stretching mode.

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Magnetic Properties of $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$: A Quasi-Ideal fcc Structure with Antiferromagnetic Ordering

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We report the magnetic properties of $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$, a bimetallic salt showing an fcc antiferromagnetic frustrated lattice. The temperature dependence of the ac magnetic susceptibility, measured on a single crystal, indicates antiferromagnetic ordering at $T_c = 0.50 \pm 0.05\text{ K}$, with a maximum at $0.80 \pm 0.01\text{ K}$. The analysis of the data gives values of $J_{nn}/k = -0.068 \pm 0.001\text{ K}$ for the first-neighbor interactions and $J_{nnn}/k = 0.005 \pm 0.001\text{ K}$ for the second-neighbor ones.

Introduction

Complex bimetallic salts have proved to be important sources of new, interesting magnetic model materials.¹ Indeed, when both complex counterions are of comparable size, the crystalline

structures of the corresponding compounds are expected to be highly isotropic. Then, it is feasible to use complex ions as building blocks of a rather symmetric crystalline lattice. When those ions are chosen carefully, it is possible to arrive at a material that exhibits magnetic ordering. Moreover, the chemistry of these compounds is quite flexible, permitting the use of a variety of

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Table I. Structural and Magnetic Data for Some Complex Bimetallic Salts

compd	space group	ordered state	T_c , K	ref
$[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$	cubic, $Fd3c$	antiferromagnetic	3.80	1
$[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$	cubic, $Pa3$	antiferromagnetic	0.50	this work
$[\text{Cr}(\text{NH}_3)_6][\text{FeCl}_6]$	cubic, $Pa3$	ferrimagnetic	1.88	3
$[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{FeCl}_6]$	cubic, $Pa3$	ferrimagnetic	2.32	2
$[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})_2][\text{FeCl}_6]$	cubic, $Pa3$	ferrimagnetic	2.31	2
$[\text{Co}(\text{NH}_3)_6][\text{NiCl}_5]$	cubic, $Fd3c$	ferrimagnetic	<1.0	3
$[\text{Co}(\text{NH}_3)_6][\text{CoCl}_4]\text{Cl}$	orthorhombic, $Pnma$	weak ferromagnetic	1.38	3
$[\text{Cr}(\text{NH}_3)_5(\text{H}_2\text{O})][\text{Cr}(\text{CN})_6]$	trigonal, $R3$	ferromagnetic	0.038	4
$[\text{Co}(\text{pn})_3][\text{FeCl}_6]^a$		antiferromagnetic	8.15	3, 5
$[\text{Cr}(\text{en})_3][\text{FeCl}_6]\text{Cl}_6 \cdot \text{H}_2\text{O}^a$	trigonal, $R3$	ferrimagnetic	0.91	2

^apn = propylenediamine; en = ethylenediamine.

metallic ions, and, therefore, large series of compounds possessing very different magnetic behavior (dia-, antiferro-, or ferrimagnets) can be prepared. As a consequence, the properties of the magnetic sublattice corresponding to each complex ion can be studied separately by choosing suitable diamagnetic counterions. Thus, we have recently reported the magnetic properties of $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$, an unusual example of a Cu derivative with three-dimensional antiferromagnetic ordering,¹ and presented data on three new ferrimagnets that order below 4.2 K.² Table I reports the structural and magnetic properties of a selected list of these types of materials.

In this paper we report the magnetic properties of $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$. As we explain below, the structure of this compound consists of two interpenetrating fcc sublattices, only one of which is formed by magnetic ions. From Mössbauer experiments, this compound had been previously described as an antiferromagnet with ordering temperature $T_c = 0.80$ K and with only first-neighbor magnetic interactions.⁶ Such a low ordering temperature is a striking feature, especially if it is compared with the related compounds shown in Table I. Moreover, the assumption of only nearest-neighbor interactions is not consistent with the crystalline symmetry of the compound.

It is worth mentioning that an fcc magnetic lattice cannot be consistent with antiferromagnetic ordering when only first-magnetic-neighbor interactions are considered. Topological restrictions preclude the onset of parallel alignment of the magnetic moments in the whole lattice, and the magnetic system becomes frustrated. Most of the work devoted to fcc antiferromagnetic ordering has been restricted to simple materials such as MnO, FeO, CoO, and NiO,⁷⁻⁹ MnS, MnSe, and MnTe,¹⁰⁻¹³ and MnS₂, MnSe₂, and MnTe₂.^{14,15} Few examples are known of coordination compounds, most of these being Ir⁴⁺ and Re⁴⁺ salts such as K₂IrCl₆ and (NH₄)₂IrCl₆,^{16,17} and K₂ReCl₆ and K₂ReBr₆.^{18,19} Therefore,

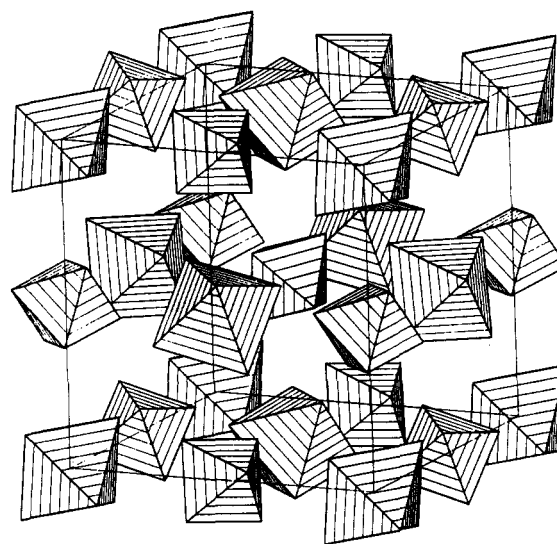


Figure 1. Crystal structure of $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$. The small octahedra correspond to the complex $[\text{Co}(\text{NH}_3)_6]^{3+}$ cations and the large ones to the complex $[\text{FeCl}_6]^{3-}$ anions.

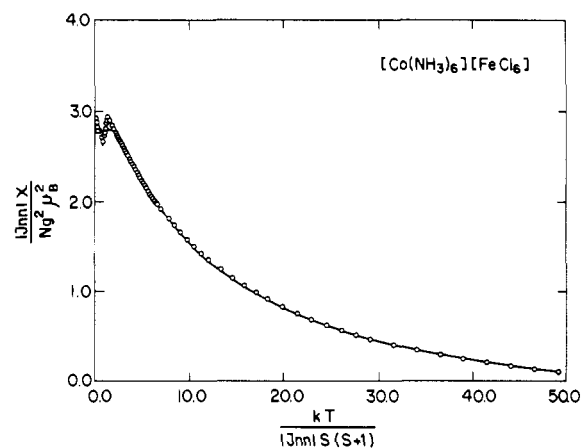


Figure 2. Experimental and fitted susceptibilities of $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$. The solid curve is the theoretical prediction for an fcc antiferromagnetic Heisenberg $S = 5/2$ model as explained in the text.

$[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$ can be considered the first example of a complex bimetallic salt showing an fcc antiferromagnetic frustrated lattice.

Experimental Section

Large single crystals of $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$ can be grown by mixing $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (1:5) in 2.5 M HCl. The solution is left to evaporate very slowly in a desiccator over a drying agent and kept at a temperature of 50 °C. These conditions are important if secondary nucleation is to be avoided. As a matter of interest, it is worth men-

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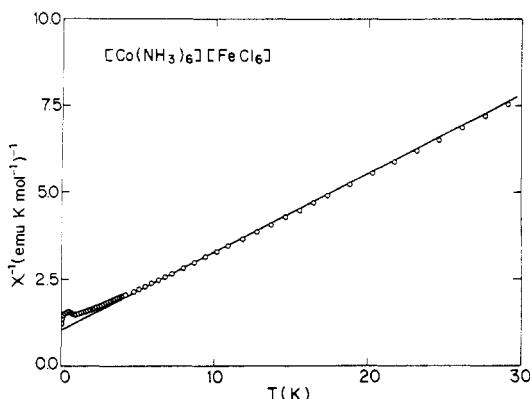


Figure 3. Ac magnetic susceptibility of $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$ plotted as χ^{-1} vs T . The straight line is the Curie-Weiss fit.

tioning that the crystal used in the measurements presented here required a year to be grown! The sample was chemically identified by elemental analysis. Anal. Calcd: Co, 13.7; Fe, 13.0; N, 19.5; H, 4.2; Cl, 49.5. Found: Co, 13.4; Fe, 12.9; N, 19.5; H, 4.1; Cl, 49.1. A crystallographic verification was made by means of a Debye-Scherrer diagram. A single crystal of 20 mg having octahedral geometry was selected for the magnetic study.

Magnetic ac susceptibility measurements in the range 1.2–30 K were conducted in a computer-controlled susceptometer.²⁰ Low temperatures down to 40 mK were attained in a commercial ^3He - ^4He dilution refrigerator; a SQUID instrument was used as a null detector.²¹

Discussion

The compound crystallizes in the cubic space group $Pa\bar{3}$ with $a = 11.2506(4)$ Å and $Z = 4$.²² The structure consists of two interpenetrating fcc sublattices, each corresponding to one of the metallic ions, as shown in Figure 1. The symmetry around each ion corresponds to an almost ideal octahedron. Around every complex ion there are six counterions at a distance $M-M'$ of $5.6253(2)$ Å, thus forming a simple cubic lattice. Each iron ion possesses twelve Fe as nearest magnetic neighbors (nn) at $7.9554(2)$ Å and six Fe as next nearest magnetic neighbors (nnn) at $11.2506(2)$ Å.

The only magnetic ion present in the compound is high-spin Fe(III), since the Co(III) ions are low spin and therefore have $S = 0$. As a consequence, the magnetic lattice corresponds to the fcc sublattice of the Fe ions. Figure 2 shows the ac magnetic susceptibility data in the temperature interval from 40 mK to 30 K. The data were taken on a single crystal with the measuring field aligned parallel to a 4-fold crystallographic axis. A maximum appears at 0.80 ± 0.01 K; then the susceptibility drops, rising again at the lowest temperatures. The increase may be due to the presence of impurities. The data correspond to the in-phase signal since no out-of-phase component was detected in the measurements. This confirms the absence of net magnetic moments in the ordered state. The data are plotted in Figure 3 as χ^{-1} vs T . The experimental data down to 4.2 K were fit to a Curie-Weiss law, yielding $C = 4.42 \pm 0.05$ emu K/mol, $g = 2.01 \pm 0.02$, and $\theta = -4.6 \pm 0.5$ K. This is to be compared to a g value of 2.0120 ± 0.0004 determined from the EPR signal of a polycrystalline powder sample of $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$ diluted in the isomorphous lattice of $[\text{Co}(\text{NH}_3)_6][\text{InCl}_6]$.²³ The negative Weiss constant is indicative of antiferromagnetic interaction between spins. The antiferromagnetic ordering temperature is about $T_c = 0.50 \pm 0.05$ K, as calculated from the maximum slope of the susceptibility curve. This result is in agreement with previous Mössbauer spectroscopy determinations except that the ordering temperature

Table II. Relation between Magnetic Frustration and Experimental Values of θ/T_c for Different Compounds

compd	θ/T_c	magnetic frustration	ref
$\text{NiBr}_2 \cdot 6\text{H}_2\text{O}$	1.8	no	34
$[\text{Cu}(\text{en})_3]\text{SO}_4^a$	1.7	no	35
$[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$	2.0	no	1
$[\text{Co}(\text{en})_3][\text{FeCl}_6]^a$	1.6	no	3
$[\text{Co}(\text{pn})_3][\text{FeCl}_6]^a$	2.0	no	3, 5
MnTe_2	5.3	yes	13
MnS_2	12.4	yes	13
$(\text{NH}_4)_2\text{IrCl}_6$	9.3	yes	12
K_2IrCl_6	10.5	yes	12
$[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$	9.2	yes	this work

^a pn = propylenediamine; en = ethylenediamine.

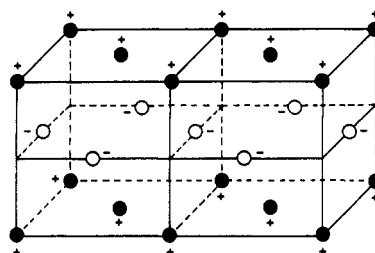


Figure 4. Representation of a type I fcc antiferromagnetic arrangement.

was estimated to be somewhat higher, at 0.80 K.⁶

Differential-scanning calorimetry measurements on the related compound $[\text{Co}(\text{NH}_3)_6][\text{CuCl}_5]$ showed that this substance undergoes a crystallographic phase transition as it cools.^{3,24} Similar measurements on $[\text{Co}(\text{NH}_3)_6][\text{FeCl}_6]$ down to 100 K have not indicated the existence of any such structural phase transition. Therefore, in the absence of a low-temperature structural determination, an fcc magnetic structure can be assumed. A characteristic of this lattice is that nn of a given site of the lattice can be nn of each other, thus forming a triangular array; therefore, straightforward antiferromagnetic alignment as found in sc and bcc lattices is just not possible. Antiparallel pairing between two nn sites will be opposed by the interactions of a third nn site of the lattice, and a magnetic frustration behavior will appear. In order to stabilize the magnetic structure, nnn interactions are required.^{25–28} It has been shown, both experimentally^{14,29} and analytically,^{30–32} that the presence of frustration reduces the critical temperature. Magnetic frustration phenomena can also appear in other types of magnetic arrangements.^{3,33} Frustrated compounds typically exhibit an unusually large θ/T_c ratio, as shown in Table II. As a consequence, mean-field theories cannot be applied for calculating the superexchange constants.³⁶

Several different kinds of magnetic structures are possible for an fcc antiferromagnetic system.^{27,37} We have explored a variety of possible structural arrangements using the high-temperature series expansions of Pirnie et al.³⁸ extrapolated with Padé-approximant techniques. The fit, reliable down to 1.1 K as shown in Figure 2, gives a value for the nn interaction of $J_{nn}/k = -0.068 \pm 0.001$ K and a value for the nnn interaction of $J_{nnn}/k = 0.005$

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± 0.001 K. A negative nn interaction together with a small and positive nnn one is characteristic of type I fcc antiferromagnetic systems.^{27,39} The magnetic structure then may consist of ferromagnetic (001) planes that are antiferromagnetically aligned with the neighboring (001) planes as represented in Figure 4. Accordingly, the magnetic moment of every ion aligns antiparallel with respect to eight first neighbors and parallel with respect to the remaining four. In addition, there are six second neighbors with their magnetic moments aligned also parallel to the central one. In other words, every ion is antiferromagnetically coupled, with two-thirds of its nn being ferromagnetically coupled with the rest of its nn plus with all its nnn.

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Neutron diffraction experiments and theoretical work are in progress in order to obtain an experimental determination of the magnetic structure and a better understanding of the magnetic behavior of this compound.

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Electrochemistry and Electrochromism of Vanadium Hexacyanoferrate

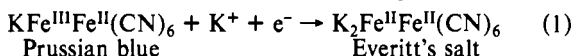
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Vanadium hexacyanoferrate (VHCF) is an electrochromic material closely related structurally to Prussian blue. The deposition, characterization, and spectroelectrochemistry of films of VHCF are reported here. The electrodeposition of VHCF films is shown to involve the reduction of vanadium(V) ion in the presence of ferricyanide ion. X-ray diffraction data confirm a cubic crystal structure for VHCF, similar to that of Prussian blue. However, chemical analyses give a higher than expected ratio of V to Fe, which suggests the presence of interstitial vanadium. While VHCF films are visually electrochromic, switching from green in the oxidized state to yellow in the reduced state, UV-vis-near-IR spectra show that most of the electrochromic modulation occurs in the ultraviolet region. From X-ray photoelectron spectroscopy and coulometric results, coupled with other electrochemical data, we conclude that the electrochromic reaction involves only the oxidation and reduction of the iron centers in the compound. The vanadium ions, found to be present predominantly in the +4 state, are unaffected by the reaction. Multiple ferrous sites are suggested to be responsible for the complex electrochemistry of VHCF.

Introduction

Electrochromic materials have received much attention recently because of their possible application in so-called "smart windows"—windows that exhibit dynamically variable light transmission characteristics.¹⁻³ One of the most durable electrochromic materials reported to date is Prussian blue, a mixed-valence compound with the nominal formula of $\text{KFe}^{\text{III}}\text{Fe}^{\text{II}}(\text{CN})_6$.⁴⁻⁶ Films of Prussian blue that have been deposited on conductive substrates can be electrochemically reduced in the presence of potassium or other alkali-metal ions, according to reaction 1, to



yield a white compound, Everitt's salt. The electrochromic reaction is quite rapid and reversible, with up to 10^7 electrochromic cycles reported for Prussian blue films electrochemically switched under appropriate conditions.⁶

An important factor in both the speed and the long-term reversibility of this electrochemical reaction is undoubtedly the relatively open crystal structure of Prussian blue. This structure features a rigid cubic framework with interstices spacious enough to easily accommodate the compensating ions involved in the reaction (i.e., K^+), thus allowing for a rapid reaction rate and minimal structural disruption.⁷ The cubic structure is formed by octahedrally coordinated Fe(III) and Fe(II), which are cyanide-bridged to yield a three-dimensional network of repeating " $-\text{NC}-\text{Fe}^{\text{II}}-\text{CN}-\text{Fe}^{\text{III}}-$ " units.

Prussian blue analogues that share this type of cubic framework are well-known. In these compounds other metal ions, typically

transition metals, replace either or both types of the iron ions in the structure.⁸⁻¹⁰ While many Prussian blue analogues are known, the electrochemical properties of only several have been studied^{4,11-16} and the electrochromic properties of still fewer have been well documented.^{11,12,15} Given the structural similarities of this family of compounds, Prussian blue analogues seem a fertile area for further electrochemical and spectroelectrochemical investigations.

Recently, the synthesis and electrochemical characterization of films of the Prussian blue analogue vanadium hexacyanoferrate (VHCF) were reported.¹⁷ The films were found to be electro-

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